

Entropy Production and Equilibrium Conditions of General-Covariant Spin Systems

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Abstract

In generalizing the special-relativistic one-component version of Eckart's continuum thermodynamics to general-relativistic space-times with Riemannian or post-Riemannian geometry¹, we consider the entropy production and other thermodynamical quantities such as the entropy flux and the Gibbs fundamental equation. We discuss equilibrium conditions in gravitational theories which are based on such geometries. In particular, thermodynamic implications of the non-symmetry of the energy-momentum tensor and the related spin balance equations are investigated, also for the special case of General Relativity.

1 Introduction

The special-relativistic version of Continuum Thermodynamics (CT) was founded by Eckart [3] in form of the special-relativistic theory of irreversible processes. CT is based (i) on the conservation law of the particle number and on the balance equation of the energy-momentum tensor and (ii) on the dissipation inequality and the Gibbs fundamental equation. In order to incorporate CT into General Relativity (GR) and other gravitational theories all based on curved space-times, as a first step, one has to go over to the general-covariant formulation of CT which is performed here.

The paper is devoted to derive the entropy production and equilibrium conditions in General-Covariant Continuum Thermodynamics (GCCT). Starting out with an entropy identity [4] –a tool to construct entropy flux and production, as well as

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¹For Riemannian and post-Riemannian geometries, see [1]. For a survey on gravitational theories based on space-times with post-Riemannian geometry, see [2]

gr-Gibbs and gr-Gibbs-Duhem equations more safely– different forms of the entropy production are considered for discussing non-dissipative materials and equilibria which both are characterized by vanishing entropy production. For defining equilibrium beyond the vanishing entropy production, additionally “supplementary equilibrium conditions” are required [4]. The material-independent equilibrium condition –that the 4-temperature vector is a Killing field– is rediscovered also for gravitational theories beyond GR including a spin part in the state space.

The paper is organized as follows: first the general-covariant shape of the energy-momentum and spin CT-balances are written down and entropy flux and production, gr-Gibbs and gr-Gibbs-Duhem equations are derived. Non-dissipative materials and equilibria of spin materials are investigated with regard to the resulting constitutive constraints. Finally, equilibrium conditions for Frenkel materials are derived.

2 General-Covariant Continuum Physics

2.1 The balance equations

The balance equations of energy-momentum and spin of phenomenological GCCT in a curved space-time² are [4]

$$\begin{aligned} T^{bc}{}_{;b} &= G^c + k^c, \quad T^{bc} \neq T^{cb}, \quad S^{cba}{}_{;c} = H^{ba} + m^{ba}, \quad (1) \\ \text{with } S^{cba} &= -S^{cab}, \quad m^{ba} = -m^{ab} \quad \text{and} \quad H^{ba} = -H^{ab}. \quad (2) \end{aligned}$$

Here, T^{ab} is the in general non-symmetric energy-momentum tensor of CT and S^{cba} the current of spin density³. The G^c and H^{bc} are internal source terms –the *Geo-SMEC-terms*⁴ [4]– which are caused by the choice of a special space time and by a possible coupling between energy-momentum, spin and geometry.

For non-isolated systems, $k^c \neq 0$ denotes an external force density, and $m^{ab} \neq 0$ is an external momentum density. As in the continuum theory of irreversible processes [5] [6], the balance equations (1) must be supplemented by those of particle number and entropy density

$$N^k{}_{;k} = 0, \quad S^k{}_{;k} = \sigma + \varphi \quad (3)$$

(N^k particle flux density, S^k entropy 4-vector, σ entropy production, φ entropy supply). The Second Law of Thermodynamics is taken into account by the demand that the entropy production has to be non-negative at each event and for arbitrary materials⁵

$$\sigma \geq 0. \quad (4)$$

²The comma denotes partial and the semicolon covariant derivatives, round brackets the symmetric part of a tensor, square brackets its asymmetric part.

³often shortly denoted as spin tensor

⁴Geometry-Spin-Momentum-Energy-Coupling

⁵after having inserted the constitutive equations into the expression of the entropy production

The (3+1)-splits of the tensors in (1) and (3) are

$$N^k = \frac{1}{c^2} n u^k, \quad n := N^k u_k, \quad (n u^k)_{;k} = 0, \quad (5)$$

$$T^{kl} = \frac{1}{c^4} e u^k u^l + \frac{1}{c^2} u^k p^l + \frac{1}{c^2} q^k u^l + t^{kl}, \quad (6)$$

$$p^l u_l = 0, \quad q^k u_k = 0, \quad t^{kl} u_k = 0, \quad t^{kl} u_l = 0, \quad (7)$$

$$S^{kab} = \left(\frac{1}{c^2} s^{ab} + \frac{2}{c^4} u^{[a} \Xi^{b]} \right) u^k + s^{kab} + \frac{2}{c^2} u^{[a} \Xi^{kb]} =: u^k \Phi^{ab} + \Psi^{kab}, \quad (8)$$

$$\Xi^b u_b = 0, \quad \Xi^{kb} u_k = \Xi^{kb} u_b = 0, \quad s^{ab} u_a = s^{ab} u_b = 0, \quad (9)$$

$$S^k = \frac{1}{c^2} s u^k + s^k, \quad s := S^k u_k, \quad s^k := h_l^k S^l. \quad (10)$$

Here, the divergence-free particle number flux density N^k is chosen according to Eckart [3], and the projector perpendicular to the 4-velocity u^k , respective u_i , is introduced

$$h_k^i = \delta_k^i - \frac{1}{c^2} u^i u_k, \quad h_k^i u_i = 0, \quad h_k^i u^k = 0, \quad (11)$$

and (9) results in

$$\Xi^b h_b^j = \Xi^j, \quad \Xi^{kb} h_k^j = \Xi^{jb}, \quad \Xi^{kb} h_b^j = \Xi^{kj}. \quad (12)$$

By splitting the stress tensor into its diagonal and its traceless parts

$$t^{kl} = -p h^{kl} + \pi^{kl}, \quad \pi^{kl} h_{kl} = 0, \quad t^{kl} h_{kl} = t_k^k =: -3p, \quad (13)$$

we introduce the pressure p and the friction tensor π^{kl} .

According to (6) and (7), we obtain

$$u_l T^{kl} = q^k + \frac{1}{c^2} e u^k. \quad (14)$$

Starting out with (8), it holds

$$\Xi^c = S^{abc} u_a u_b, \quad \Xi^{mc} = S^{abc} h_a^m u_b, \quad (15)$$

resulting in

$$\Xi^{mc} + \frac{1}{c^2} \Xi^c u^m = S^{mbc} u_b. \quad (16)$$

Taking (12) into account, we obtain

$$S^{mbc} u_b h_c^j = S^{mbj} u_b. \quad (17)$$

2.2 The entropy identity

For establishing the entropy balance equation, we use a special procedure starting out with an identity [4], the so-called *entropy identity*. This results by multiplying (5)₁, (14) and (16) with for the present arbitrary quantities κ , λ and Λ_c –which are suitably chosen below– (10)₁ becomes

$$S^k \equiv \frac{1}{c^2}su^k + s^k + \kappa\left[N^k - \frac{1}{c^2}nu^k\right] + \lambda\left[u_l T^{kl} - q^k - \frac{1}{c^2}eu^k\right] + \Lambda_c\left[S^{kbc}u_b - \Xi^{kc} - \frac{1}{c^2}\Xi^c u^k\right] = \quad (18)$$

$$= \frac{1}{c^2}su^k - \kappa\frac{1}{c^2}nu^k - \lambda\frac{1}{c^2}eu^k - \frac{1}{c^2}\Lambda_c\Xi^c u^k + \kappa N^k + \lambda u_l T^{kl} + \Lambda_c S^{kbc}u_b + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc}\right). \quad (19)$$

This entropy identity does not take the entire energy-momentum and spin tensor into account, but only their contractions with u_l according to (18). This means, that the contractions with h_{kl} are not included in the entropy identity resulting in the consequence that more than one entropy identity can be established, if other secondary conditions are taken into consideration. Consequently, also the results received by exploiting the entropy identity are not unique, but depend on the chosen entropy identity. Here, we start out with (18).

Because the part of Λ_c which is parallel to u^c does not contribute to the last term of (18) –and consequently not to the entropy identity– we can demand

$$\Lambda_c u^c \doteq 0 \quad (20)$$

without restricting the generality. The identity (19) becomes another one by differentiation

$$S^k{}_{;k} \equiv \left[\frac{1}{c^2}(s - \kappa n - \lambda e - \Lambda_c \Xi^c)u^k\right]_{;k} + \left(\kappa N^k\right)_{;k} + \left(\lambda u_m T^{km}\right)_{;k} + \left(\Lambda_c S^{kbc}u_b\right)_{;k} + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc}\right)_{;k}. \quad (21)$$

This identity changes into the entropy production, if according to (3)₂ and (10)₁, s , s^k and φ are specified. For achieving that, we now transform the five terms of (21).

Introducing the time derivative⁶ and implying the balance equations (3)₁ and

⁶ $\dot{\boxplus} := \boxplus_k u^k$ is the relativistic analogue to the non-relativistic material time derivative $d\boxplus/dt$ which describes the time rates of a rest-observer. Therefore, $\dot{\boxplus}$ is observer-independent and zero in equilibrium [7] [8].

(1)_{1,3}, the entropy identity (21) becomes

$$\begin{aligned}
S^k{}_{;k} \equiv & \frac{1}{c^2} \left(\dot{s} - \dot{\kappa} n - \dot{\kappa} \dot{n} - \dot{\lambda} e - \dot{\lambda} \dot{e} - \dot{\Lambda}_c \Xi^c - \Lambda_c \dot{\Xi}^c \right) + \\
& + \frac{1}{c^2} \left(s - \kappa n - \lambda e - \Lambda_c \Xi^c \right) u^k{}_{;k} + \kappa_{;k} \frac{1}{c^2} n u^k + \\
& + \left(\lambda u_m \right)_{;k} T^{km} + \lambda u_m (G^m + k^m) + \\
& + \left(\Lambda_c u_b \right)_{;k} S^{kbc} + \Lambda_c u_b (H^{bc} + m^{bc}) + \\
& + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc} \right)_{;k}. \tag{22}
\end{aligned}$$

Taking (14), (6) and (13) into account, the fourth term of (22) becomes

$$\begin{aligned}
\left(\lambda u_m \right)_{;k} T^{km} &= \lambda_{,k} \left(q^k + \frac{1}{c^2} e u^k \right) + \lambda u_{m;k} \left(\frac{1}{c^2} u^k p^m - p h^{km} + \pi^{km} \right) = \\
&= \lambda_{,k} q^k + \frac{1}{c^2} \dot{\lambda} e + \frac{1}{c^2} \lambda \dot{u}_m p^m - \lambda p u^k{}_{;k} + \lambda u_{m;k} \pi^{km}. \tag{23}
\end{aligned}$$

We now transform the sixth term of the entropy identity (22) by taking (8) and (20) into account

$$\begin{aligned}
\left(\Lambda_c u_b \right)_{;k} S^{kbc} &= \left(\Lambda_c u_b \right) \dot{\Phi}^{bc} + \left(\Lambda_c u_b \right)_{;k} \Psi^{kbc} = \\
&= \left(\dot{\Lambda}_c u_b + \Lambda_c \dot{u}_b \right) \left(\frac{1}{c^2} s^{bc} + \frac{1}{c^4} (u^b \Xi^c - u^c \Xi^b) \right) + \\
&+ \left(\Lambda_{c;k} u_b + \Lambda_c u_{b;k} \right) \left(s^{kbc} + \frac{1}{c^2} (u^b \Xi^{kc} - u^c \Xi^{kb}) \right) = \\
&= \dot{\Lambda}_c \frac{1}{c^2} \Xi^c + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc}. \tag{24}
\end{aligned}$$

Inserting (23) and (24) into (22) results in

$$\begin{aligned}
S^k{}_{;k} \equiv & \frac{1}{c^2} \left(\dot{s} - \dot{\kappa} n - \dot{\kappa} \dot{n} - \dot{\lambda} e - \dot{\lambda} \dot{e} - \dot{\Lambda}_c \Xi^c \right) + \\
& + \frac{1}{c^2} \left(s - \kappa n - \lambda e - \Lambda_c \Xi^c - \lambda c^2 p \right) u^k{}_{;k} + \\
& + \lambda_{,k} q^k + \frac{1}{c^2} \lambda \dot{u}_m p^m + \lambda u_{m;k} \pi^{km} + \lambda u_m (G^m + k^m) + \\
& + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc} + \Lambda_c u_b (H^{bc} + m^{bc}) + \\
& + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc} \right)_{;k} \equiv \sigma + \varphi. \tag{25}
\end{aligned}$$

As already mentioned, the entropy identity has to be transferred into the expression for the entropy production by specifying the entropy flux s^k , the entropy density s , the entropy supply φ and the three for the present arbitrary quantities κ , λ and Λ_c .

Obviously, (25) contains terms of different kind: a divergence of a vector perpendicular to u^k (the last term of (25)), time derivatives of intensive quantities (the first row of (25)), two terms stemming from the field equations (last terms of the third and fourth row of (25)), three terms containing spin (3+1)-components (in the fourth row of (25)) and three further terms containing (3+1)-components of the energy-momentum tensor (in the third row of (25)). This structure of the entropy identity allows to choose a state space and by virtue of it, to define the entropy density, the entropy supply, the entropy flux, the gr-Gibbs equation and the gr-Gibbs-Duhem equation which all are represented in the next sections.

2.3 The entropy supply

If the system under consideration is isolated, the external sources vanish

$$k^m \doteq 0, \quad m^{bc} \doteq 0, \quad (26)$$

and with them also the *entropy supply*

$$\varphi \equiv 0. \quad (27)$$

Thus, because the entropy supply is generated by external sources, we define

$$\varphi := \lambda u_m k^m + \Lambda_c u_b m^{bc}. \quad (28)$$

2.4 State space, gr-Gibbs equation and entropy flux

We now choose a *state space* which belongs to a one-component spin system in local equilibrium⁷ and which is spanned by the particle number n , the energy density e and the spin density vector Ξ_c

$$\boxplus = (n, e, \Xi_c). \quad (29)$$

According to (15) and (16), the 3-indexed spin is only partly taken into account, namely by Ξ_c and Ξ^{kc} . Here, Ξ_c is an independent state variable, whereas Ξ^{kc} represents a constitutive property according to (34).

The *gr-Gibbs equation* is given by the relativistic time derivative of the entropy density s which is composed of time derivatives belonging to the chosen state space. Such time derivatives appear only in the first row of (25)⁸. Consequently, we define

$$\dot{s} := \kappa \dot{n} + \lambda \dot{e} + \Lambda_c \dot{\Xi}^c. \quad (30)$$

⁷Local equilibrium means: The state at each event is described by a set of equilibrium variables which change from event to event generating gradients of equilibrium variables causing irreversible processes.

⁸The acceleration \dot{u}_m is not a material property, but one of the kinematical invariants.

Up to here, the quantities κ , λ , Λ_c introduced into the entropy identity (18) are unspecified. Taking the gr-Gibbs equation (30) into consideration, such a specification is now possible: λ is the reciprocal rest-temperature

$$\lambda := \frac{1}{T}, \quad (31)$$

κ is proportional to the chemical potential

$$\kappa := -\frac{\mu}{T}, \quad (32)$$

and Λ_c is analogous to (32) proportional to a spin potential

$$\Lambda_c := -\frac{\mu_c}{T}. \quad (33)$$

These quantities as all the others which do not belong to the state space variables (29) are constitutive quantities describing the material by constitutive equations. These constitutive quantities are

$$\mathbf{M} = (T, \mu, \mu_c, p^k, q^k, p, \pi^{km}, s^{km}, s^{ckm}, \Xi^{km}). \quad (34)$$

They all –including the entropy density s and the entropy flux density s^k – are functions of the state space variables

$$\mathbf{M} = \mathcal{M}(\boxplus). \quad (35)$$

These *constitutive equations*⁹ are out of scope of this paper.

Because of (31), the term λq^k is as in CT a part of the entropy flux. Consequently, we define the *entropy flux* according to the last row of (25)

$$s^k := \lambda q^k + \Lambda_c \Xi^{kc}. \quad (36)$$

According to (34), the entropy flux density is also a constitutive quantity.

2.5 Entropy density and gr-Gibbs-Duhem equation

According to the second row of the entropy identity (25), we define the *entropy density*

$$s := \kappa n + \lambda e + \Lambda_c \Xi^c + \lambda c^2 p. \quad (37)$$

This definition has to be in accordance with the gr-Gibbs equation (30). As usual in non-relativistic thermostatics, we demand a *gr-Gibbs-Duhem equation* of the intensive variables

$$\dot{\kappa} n + \dot{\lambda} (e + c^2 p) + \dot{\Lambda}_c \Xi^c + \lambda c^2 \dot{p} = 0. \quad (38)$$

⁹How to use the constitutive equations in connection with the gravitational field equations (1) see [9].

2.6 The entropy production

Inserting the entropy supply (28), the entropy flux (36), the gr-Gibbs equation (30) and the entropy density (37) into the entropy identity (25), we obtain the *entropy production*

$$\begin{aligned}\sigma = & \lambda_{,k}q^k + \frac{1}{c^2}\lambda \dot{u}_m p^m + \lambda u_{m;k}\pi^{km} + \lambda u_m G^m + \\ & + \Lambda_c \dot{u}_b \frac{1}{c^2}s^{bc} + \Lambda_{c;k}\Xi^{kc} + \Lambda_c u_{b;k}s^{kbc} + \Lambda_c u_b H^{bc}.\end{aligned}\quad (39)$$

We get by taking (7)₁ and (10)₃ into account

$$\frac{1}{c^2}\lambda \dot{u}_m p^m + \Lambda_c \dot{u}_b \frac{1}{c^2}s^{bc} = -\frac{1}{c^2}u_m \left(\lambda \dot{p}^m + \Lambda_c \dot{s}^{mc} \right). \quad (40)$$

Putting together

$$\begin{aligned}-\frac{1}{c^2}u_m \left(\lambda \dot{p}^m + \Lambda_c \dot{s}^{mc} \right) + \lambda u_m G^m + \Lambda_c u_b H^{bc} = \\ = u_m \left[\lambda \left(G^m - \frac{1}{c^2}\dot{p}^m \right) + \Lambda_c \left(H^{mc} - \frac{1}{c^2}\dot{s}^{mc} \right) \right],\end{aligned}\quad (41)$$

the entropy production (39) results in

$$\begin{aligned}\sigma = & \lambda_{,k}q^k + \Lambda_{c;k}\Xi^{kc} + u_{m;k} \left(\lambda \pi^{km} + \Lambda_c s^{kmc} \right) + \\ & + u_m \left[\lambda \left(G^m - \frac{1}{c^2}\dot{p}^m \right) + \Lambda_c \left(H^{mc} - \frac{1}{c^2}\dot{s}^{mc} \right) \right],\end{aligned}\quad (42)$$

an expression which belongs to a general-covariant one-component spin system. The entropy production depends on the Geo-SMEC-terms of the balance equations, that means, the same material has different entropy productions in space-times of different theories. Entropy flux and -density, gr-Gibbs and gr-Gibbs-Duhem equation do not depend on Geo-SMEC-terms because energy-momentum and spin tensor are independent of the Geo-SMEC-terms¹⁰.

3 Further Forms of Entropy Production

The gradient of the velocity can be decomposed into its kinematical invariants: symmetric traceless shear σ_{nm} , expansion Θ , anti-symmetric rotation ω_{nm} and acceleration \dot{u}_n [10]

$$u_{l;k} = \sigma_{lk} + \omega_{lk} + \Theta h_{lk} + \frac{1}{c^2}\dot{u}_l u_k, \quad (43)$$

$$\sigma_{lk} = \sigma_{kl}, \quad \omega_{lk} = -\omega_{kl}, \quad u^l \sigma_{lk} = \sigma_{lk} u^k = u^l \omega_{lk} = \omega_{lk} u^k = 0, \quad (44)$$

$$\sigma_k^k = \omega_k^k = 0, \quad \Theta := u_k^k. \quad (45)$$

¹⁰That is obvious, because the (3+1)-splits (6) and (8) are valid for all space-times.

Consequently, the third term of (39) can be replaced by

$$\lambda u_{m;k} \pi^{km} = \lambda \sigma_{mk} \pi^{(km)} + \lambda \omega_{mk} \pi^{[km]}. \quad (46)$$

We now derive another shape of the entropy production: Starting out with the entropy identity (21), we obtain the entropy production by taking the entropy flux (36), the entropy density (37) and the energy-momentum balance (1)₁, the particle balance (3)₁ and (5)₁ into account. Inserting these quantities, we obtain for isolated systems

$$\sigma = \frac{1}{c^2} \left[\lambda c^2 p u^k \right]_{;k} + \dot{\kappa} \frac{1}{c^2} n + (\lambda u_m)_{;k} T^{km} + \lambda u_m G^m + \left(\Lambda_c u_b S^{kbc} \right)_{;k}, \quad (47)$$

and the first term of (47) is

$$\frac{1}{c^2} \left[\lambda c^2 p u^k \right]_{;k} = (\lambda p)^\bullet + \lambda p u^k_{;k}. \quad (48)$$

For the sequel, we need an additional expression whose validity is independent of the entropy production because it represents an identity

$$\begin{aligned} (\lambda u_m)_{;k} \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right) &= (\lambda_{,k} u_m + \lambda u_{m;k}) \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right) = \\ &= \frac{e}{c^2} \lambda^\bullet - \lambda p u^k_{;k}. \end{aligned} \quad (49)$$

The sum of (47) and (49) results in

$$\begin{aligned} \sigma &= (\lambda p)^\bullet + \frac{e}{c^2} \lambda^\bullet + \dot{\kappa} \frac{1}{c^2} n + \\ &+ (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \\ &+ \lambda u_m G^m + \left(\Lambda_c u_b \right)_{;k} S^{kbc} + \Lambda_c u_b H^{bc}. \end{aligned} \quad (50)$$

Replacing the first two terms by the gr-Gibbs-Duhem equation (38), we obtain by taking (24) into account

$$\begin{aligned} \sigma &= -\frac{1}{c^2} \dot{\Lambda}_c \Xi^c + (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \\ &+ \lambda u_m G^m + \left(\Lambda_c u_b \right)_{;k} S^{kbc} + \Lambda_c u_b H^{bc} = \end{aligned} \quad (51)$$

$$\begin{aligned} &= (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \lambda u_m G^m + \\ &+ \Lambda_c u_b \left(H^{bc} - \frac{1}{c^2} \dot{s}^{bc} \right) + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} S^{kbc}. \end{aligned} \quad (52)$$

Here in contrast to (42), the heat flux q^k and the friction tensor π^{km} do not appear. They are replaced by the first term of (52) describing the deviation

of the material from a perfect one. The second row represents the influence of the chosen state space (29) on the entropy production introduced by the third term of (18).

We now consider the thermodynamical results: if we start out with the entropy identity for which third term of (18) is set to zero $\Lambda_c \equiv 0$ [11]. That means, we change the state space (29) into

$$\Xi_0 = (n, e). \quad (53)$$

The entropy production (52) becomes

$$\sigma_0 = (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \lambda u_m G^m, \quad (54)$$

and the entropy flux (36) is

$$s_0^k = \lambda q^k. \quad (55)$$

The gr-Gibbs equation (30) becomes

$$\dot{s}_0 = \kappa \dot{n} + \lambda \dot{e}, \quad (56)$$

and the entropy density (37) is

$$s_0 = \kappa n + \lambda e + c^2 \lambda p. \quad (57)$$

Finally, the gr-Gibbs-Duhem equation (38) results in

$$\dot{\kappa} n + \dot{\lambda} (e + c^2 p) + \dot{p} c^2 \lambda = 0. \quad (58)$$

The thermodynamical quantities (54) to (58) base on the chosen state space as a comparison with (30), (29), (37) and (38) demonstrates. Consequently, the thermodynamical quantities are not "absolute", they belong to a thermodynamical scheme implemented by a chosen state space. The spin does not appear in the thermodynamical quantities (54) to (58) in contrast to (30), (29), (37) and (38). Also the regard of the spin balance (1)₃ is different: the entropy production (52) takes it explicitly into account, whereas spin parts do not appear in (54) [12]. Here, the spin is a constitutive quantity and not a state space variable. For the sequel, we use the state space (29) because of its generality and consider the restricted state space (53) as a special case.

The special case (53) can be easily obtained by the setting $\Lambda_c \doteq 0$. Especially in GR, the energy-momentum tensor is symmetric and the external sources and the Geo-SMEC-terms are zero. Thus (52) results in

$$\sigma_0^{GR} = \frac{1}{2} \left[(\lambda u_m)_{;k} + (\lambda u_k)_{;m} \right] \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right). \quad (59)$$

Consequently, the entropy production vanishes in GR for perfect materials or/and if the spacetime allows that the 4-temperature vector is a Killing field. This is the well-known result derived in [12] which is here worked out using a more general aspect. More details in connection with equilibrium will be discussed in sect.5.1.

4 Non-dissipative Materials

As already mentioned, the entropy production is always connected with a chosen state space. Thus (52) belongs to (29), and (54) to (53): the entropy production depends on the material and on the space-time, a statement which is also valid for its zero. A *non-dissipative material* is characterized by vanishing entropy production (52) even in the case of non-equilibrium¹¹ independently of the specially chosen space-time. Consequently by definition, all processes of non-dissipative materials are reversible¹², and therefore these materials are those of thermostatics. If the state space is changed, it may be that a non-dissipative material becomes dissipative.

Starting out with (52), we point out a set of conditions which is sufficient that a material is non-dissipative, that means, its entropy production vanishes independently of the space-time. These conditions are generated by setting individual terms in (52) to zero. First the non-dissipative material is perfect

$$T_{\text{ndiss}}^{kl} \doteq \frac{1}{c^4} e u^k u^l - p h^{kl}, \quad \longrightarrow \quad T_{\text{ndiss}}^{[kl]} = 0, \quad (60)$$

for which the first term of (52) vanishes. Also the second term must vanish

$$G_{\text{ndiss}}^m \doteq 0, \quad (61)$$

that means, the Geo-SMEC-term of the energy-momentum balance has to be zero.

The second row of (52) depends on Λ_c which introduces according to the last term of (18) a spin part explicitly into the state space (29). There are now two possibilities for vanishing the second row of (52): first

$$H_{\text{ndiss}}^{bc} = 0, \quad \dot{s}_{\text{ndiss}}^{bc} = 0, \quad \Psi_{\text{ndiss}}^{kbc} = 0, \quad (62)$$

or second

$$\Lambda_c^{\text{ndiss}} = 0. \quad (63)$$

If now Λ_c vanishes in (52) –and consequently also in (18)– spin terms cannot appear in the state space, with the result that we have to choose the state space (53) instead of (29).

Finally, we proved two statements which presupposes different state spaces for non-dissipative materials.

■ **Proposition I:** The five altogether sufficient conditions characterizing non-dissipative materials are: (i) the material is perfect, (ii) the Geo-SMEC-terms of the energy-momentum and of the spin balance vanish, (iii) the spin is $S_{\text{ndiss}}^{kbc} = u^k \Phi_{\text{ndiss}}^{bc}$, (iv) the spin density (62)₂ is covariantly constant and (v)

¹¹Vanishing entropy production is necessary, but not sufficient for equilibrium.

¹²Reversible "processes" are trajectories in the state space consisting of equilibrium states.

the state space is spanned by the particle number, the energy density and the spin density vector Ξ_c . ■

The second proposition presupposing the state space (53) is as follows:

■ **Proposition II:** The three altogether sufficient conditions characterizing non-dissipative materials are: (i) the material is perfect, (ii) the Geo-SMEC-term of the energy-momentum balance vanishes, (iii) the state space is spanned by the particle number and the energy density. ■

5 Equilibrium

5.1 Equilibrium Conditions

We start out with the question: How are equilibrium and non-dissipative materials related to each other? Concerning non-dissipative materials, we are looking for material properties enforcing vanishing entropy production for all admissible space-times. Concerning equilibria, we are asking for space-times in which materials can be at equilibrium. This is defined by *equilibrium conditions* which are divided into necessary and supplementary ones [4]. The necessary ones are given by vanishing entropy production and vanishing entropy flux density

$$\sigma^{eq} \doteq 0 \quad \wedge \quad s_{eq}^k \doteq 0. \quad (64)$$

Supplementary equilibrium conditions are given by vanishing material time derivatives, except that of the 4-velocity

$$\boxplus_{eq}^\bullet \doteq 0, \quad \boxplus \neq u^l. \quad (65)$$

Consequently according to (30) and (38), the gr-Gibbs and the gr-Gibbs-Duhem equations are identically satisfied in equilibrium. Whereas in sect.4 the non-dissipative materials are defined independently of the admissible space-times, here a material in a given space-time is considered and the equilibrium conditions (64) and (65) are valid.

From (3)₁ follows

$$\dot{n} := n_{,k} u^k = -n u^k_{;k} \longrightarrow u^k_{;k} = -\frac{\dot{n}}{n}. \quad (66)$$

According to (66)₃ and (65)₁, the divergence of the 4-velocity –that is the expansion (45)₂– vanishes always in equilibrium¹³

$$u^k_{;k}{}^{eq} = 0. \quad (67)$$

¹³for arbitrary space-times and materials

Starting out with the identity (49) and taking (65) and (67) into account, we obtain for all equilibria

$$(\lambda u_m)_{;k}^{eq} \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right)^{eq} = 0. \quad (68)$$

Because the second bracket of (68) is never zero, the 4-temperature vector λu_m is independently of the material a Killing vector in equilibrium

$$\left[(\lambda u_m)_{;k} + (\lambda u_k)_{;m} \right]^{eq} = 0. \quad (69)$$

The equilibrium conditions (67) and (69) are induced by (65)₁ independently of the entropy production and the material. No equilibria are possible in space-times which do not allow the validity of (67) or/and (69). Obvious is that the conditions (67) and (69) are necessary, but not sufficient for equilibrium, because they do not guarantee vanishing entropy production (52) or (54), except for the case of GR according to (59). Hence, vanishing entropy production in GR means two different things: the system may be in equilibrium¹⁴ or the system is non-dissipative and reversible processes occur.

The expression of the entropy production (42) becomes in equilibrium by taking (46) into account

$$\begin{aligned} 0 = & \lambda_{,k}^{eq} q_{eq}^k + \Lambda_{c;k}^{eq} \Xi_{eq}^{kc} + \\ & + \sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) + \omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) + \\ & + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right). \end{aligned} \quad (70)$$

From (36) and (64)₂ follows

$$q_{eq}^k = -\frac{1}{\lambda^{eq}} \Lambda_c^{eq} \Xi_{eq}^{kc} \longrightarrow \lambda_{,k}^{eq} q_{eq}^k = -\frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \Xi_{eq}^{kc}. \quad (71)$$

Inserting (71) into (44) results in

$$\begin{aligned} 0 = & \Xi_{eq}^{kc} \left(\Lambda_{c;k}^{eq} - \frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \right) + \\ & + \sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) + \omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) + \\ & + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right). \end{aligned} \quad (72)$$

In contrast to the material-independent equilibrium conditions (67) and (69), the equilibrium conditions (70) to (72) depends on material and space-time. Each of these three condition is necessary for equilibrium, and altogether they are sufficient for equilibrium because the field equations (1) and the entropy

¹⁴if all the other equilibrium conditions are valid

supply (28) are taken into account.

An other shape of (72) can be derived from (52) by taking (69) into account

$$0 = (\lambda u_m)_{;k}^{eq} T_{eq}^{[km]} + \Lambda_{c;k}^{eq} \Xi_{eq}^{kc} + \Lambda_c^{eq} u_{m;k}^{eq} s_{eq}^{kmc} + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right). \quad (73)$$

This equilibrium condition is satisfied in GR because the energy-momentum tensor is symmetric, both Geo-SMEC-term vanishes and the state space (53) is used. General solutions of (72) and (73), that means, to find all couples –material \leftrightarrow space time– which satisfy (72) and (73), cannot be achieved. Therefore, we discuss some special cases of equilibria in the next section.

5.2 Special equilibria

We now decompose the equilibrium condition (72) into a set of terms representing special cases of equilibria and which altogether enforce the validity of (72):

$$\Xi_{eq}^{kc} \left(\Lambda_{c;k}^{eq} - \frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \right) \doteq 0, \quad (74)$$

$$\sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) \doteq 0, \quad (75)$$

$$\omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) \doteq 0, \quad (76)$$

$$u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right) \doteq 0. \quad (77)$$

If we do not restrict the spin material under consideration, the bracket in (74) has to be zero resulting in a differential equation for the spin potential (33)

$$\lambda^{eq} \Lambda_{c;k}^{eq} - \lambda_{,k}^{eq} \Lambda_c^{eq} = 0. \quad (78)$$

Because this equilibrium condition is pretty exotic, we restrict our discussion to spin materials with vanishing Ξ^{kc} . According to (8) and (71), we obtain

$$\Xi^{kc} \doteq 0, \quad \longrightarrow \quad S^{kbc} = u^k \Phi^{bc} + s^{kbc} \quad \wedge \quad q_k^{eq} = 0. \quad (79)$$

According to (75) and (76), the couple stress s^{kbc} modifies the friction tensor

$$\Pi_{eq}^{km} := \lambda^{eq} \pi_{eq}^{km} + \Lambda_c^{eq} s_{eq}^{kmc}, \quad (80)$$

and necessary material-independent equilibrium conditions are

$$\sigma_{mk}^{eq} = 0, \quad \omega_{mk}^{eq} = 0. \quad (81)$$

Another necessary equilibrium condition is (77). In connexion with (73), we obtain

$$(\lambda u_m)_{;k}^{eq} T_{eq}^{[km]} + \Lambda_c^{eq} u_{m;k}^{eq} s_{eq}^{kmc} = 0, \quad (82)$$

a relation which is satisfied, if we have e.g.

$$(\lambda u_m)_{;k}^{eq} = 0 \quad \wedge \quad s_{eq}^{kmc} = 0. \quad (83)$$

Using the state space (53), (74) to (77) result in (81) or

$$\pi_{eq} = 0 \quad \wedge \quad u_m^{eq} G_{eq}^m = 0. \quad (84)$$

5.3 Frenkel materials

Materials defined by the special spin¹⁵

$$\Psi_{\text{FR}}^{kbc} \doteq 0 \quad \wedge \quad \left[\Phi_{\text{FR}}^{bc} u_b \doteq 0 \quad \longrightarrow \quad \Xi_{\text{FR}}^c = 0 \right] \quad (85)$$

are called *Frenkel materials*. According to (85)₂, Frenkel materials belong to the state space (53), and their spin is

$$S_{\text{FR}}^{kbc} = u^k s^{bc}. \quad (86)$$

According to (52), a necessary equilibrium condition of Frenkel materials is

$$0 = (\lambda u_m)_{;k}^{eq} \left(T_{\text{FR}}^{km} - \frac{1}{c^4} e_{\text{FR}} u^k u^m + p h_{\text{FR}}^{km} \right)^{eq} + u_m^{eq} \lambda^{eq} G_{\text{FReq}}^m. \quad (87)$$

If the Frenkel material is dissipative, the equilibrium conditions are (67), (69) and according to (87)

$$(\lambda u_m)_{;k}^{eq} T_{\text{FReq}}^{[km]} = 0, \quad u_m^{eq} \lambda^{eq} G_{\text{FReq}}^m = 0, \quad (88)$$

and additionally according to (71)₁ and (75)/(76)

$$q_{\text{FReq}}^k = 0, \quad \sigma_{mk}^{eq} \lambda^{eq} \pi_{\text{FReq}}^{(km)} = 0, \quad \omega_{mk}^{eq} \lambda^{eq} \pi_{\text{FReq}}^{[km]} = 0. \quad (89)$$

6 Discussion

Starting out with the entropy identity derived in [4] and specifying entropy flux, entropy density and entropy supply, different expressions of the entropy production in general-relativistic space-times are determined by taking the gr-Gibbs and the gr-Gibbs-Duhem equations into regard. All these thermodynamical quantities depend on the chosen state space which in general is more extended than that of General Relativity. Beyond that, the entropy production of a general-covariant one-component spin system depends on the so-called Geo-SMEC-terms which are located at the rhs of the balance equations, thus discriminating between different general-covariant theories.

¹⁵taking (9)₃into account

Well-known relations of General Relativity are generalized for theories based on post-Riemannian space-times. In this case, the interrelation between geometric and constitutive quantities in the expression for the entropy production becomes more complex. Consequently, the zero of the entropy production can be realized by a variety of conditions imposed on constitutive and/or geometric quantities. One condition of them is the fact that the entropy production vanishes for perfect materials, if the state space does not include spin terms and if the Geo-SMEC-term of the energy-momentum balance is zero. That is just the well-known case of General Relativity.

Vanishing of entropy production is only necessary, but not sufficient for equilibrium. This necessary condition has to be complemented by "supplementary equilibrium conditions" for describing equilibrium sufficiently. Two supplementary equilibrium conditions are independent of the entropy production restricting the space-time independently of the material: the expansion vanishes and the 4-temperature vector is a Killing field. Equilibria are impossible, if one of these conditions is not satisfied.

From the viewpoint of material theory, the conditions are interesting for which the entropy production vanishes whatever the properties of the space-time of the considered theory may be. One set of conditions for non-dissipativity is: the material is perfect, the Geo-SMEC-term of the energy-momentum balance vanishes and the state space is spanned by particle number and energy density. That is again the special case of General Relativity.

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